

992,359



PATENT SPECIFICATION

NO DRAWINGS

992,359

Date of Application and filing Complete Specification: May 14, 1963.

No. 19161/63.

Application made in Germany (No. C26983 IVd/39b) on May 14, 1962.

Application made in Germany (No. C27790 IVd/39b) on Aug. 27, 1962.

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PATENTS ACT, 1949

SPECIFICATION NO. 992,359

The following amendments were allowed under Section 29 on 21st October 1968.

Page 1, lines 36 and 51, page 2, line 11, page 9, lines 4 and 17, delete "compounds" insert "hydrocarbons"

THE PATENT OFFICE,
11th December 1968

D 10945

10 ments in and relating to crosslinking and is particularly concerned with improvements in and relating to the vulcanization of unsaturated copolymers.

It has been proposed in Patent Specifications Nos. 879,232 and 892,462 to vulcanize elastomers such as butyl rubber, acrylonitrile - butadiene rubber and butadiene styrene rubber by means of phenolic resins in the presence of one or more halides of metals of Group II or Group III of the Periodic Table or of heavy metals. According to Patent Specifications Nos. 892,462; 912,975 and 921,511 these metal halides may be produced *in situ* from halogen-donors, for example organic compounds such as chlorosulphonated polyethylene or polychloroprene, and from metal oxides or metal salts of weak acids respectively.

According to the invention there is provided a process for cross-linking unsaturated copolymers comprising vulcanizing one or more copolymers, which have been obtained by the copolymerisation of one or more polyolefinically unsaturated compounds having 4 to 14 carbon atoms and which may have a cyclic structure with one or more straight-chain monolefinic compounds having 2 to 10 carbon atoms by one or more phenol resins, as herein defined, in the presence of one or more halides, preferably chlorides, of one or more metals of Groups II or III of the Periodic Table or halides of a heavy metal, said heavy metal having a specific gravity greater than 4 or a mixture of halide precursors for any such halide or halides as herein defined. The Periodic Table used is that of Lothar Meyer

[Pr

containing up to 90 mol per cent, calculated on the total mono-olefin component, of one or more branched mono-olefinic hydrocarbons having 4 to 12 carbon atoms.

The fact that such copolymers may be cross-linked according to the invention by the substances in question is fundamentally new and very important insofar as these copolymers have properties completely different from butyl rubber and other elastomers. For example, they are quite different from butyl rubber in that they are very much less branched. The copolymers to be cross-linked according to the invention may contain double bonds either in the main chains or in side chains.

The polyolefinically unsaturated compound may be cyclic or acyclic or mixtures of such compounds. The proportion of cyclic compound in the polyolefinically unsaturated compound mixture may be at least 10, preferably at least 50 mol per cent. Usually these compounds will be dienes and, moreover, preferably those having conjugated double bonds. The polyolefinically unsaturated compound may contain the group $\text{CH}_2=\text{C}<$.

Specific examples of acyclic dienes have the formula $\text{CH}_2=\text{CH}-\text{CR}^1=\text{CH}_2$ in which R^1 is hydrogen, methyl, ethyl, propyl, chlorine, fluorine, acetoxy, chloroacetoxy, butyroxyl or cyano radical, e.g. butadiene, isoprene, 2,3 - dimethyl - butadiene - 1,3, 1,2 - dimethyl - butadiene - 1,3, 1,3 - dimethyl - butadiene - 1,3, 1,4 - dimethyl - butadiene - 1,3, 1 - ethyl - butadiene - 1,3, 2 - ethylbutadiene - 1,3, 2 - propylbutadiene - 1,3, 2 - chlorobutadiene - 1,3, 2 - fluoro - butadiene - 1,3, 2 - acetoxy - butadiene - 1,3, 2 - chloroacetoxy - butadiene -



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Int. Cl.:—C 08 d

COMPLETE SPECIFICATION

Improvements in or relating to Cross-Linking of Unsaturated Copolymers

We, CHEMISCHE WERKE ALBERT, a German Body Corporate of Wiesbaden-Biebrich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in and relating to crosslinking and is particularly concerned with improvements in and relating to the vulcanization of unsaturated copolymers.

It has been proposed in Patent Specifications Nos. 879,232 and 892,462 to vulcanize elastomers such as butyl rubber, acrylonitrile-butadiene rubber and butadiene styrene rubber by means of phenolic resins in the presence of one or more halides of metals of Group II or Group III of the Periodic Table or of heavy metals. According to Patent Specifications Nos. 892,462; 912,975 and 921,511 these metal halides may be produced *in situ* from halogen-donors, for example organic compounds such as chlorosulphonated polyethylene or polychloroprene, and from metal oxides or metal salts of weak acids respectively.

According to the invention there is provided a process for cross-linking unsaturated copolymers comprising vulcanizing one or more copolymers, which have been obtained by the copolymerisation of one or more polyolefinically unsaturated compounds having 4 to 14 carbon atoms and which may have a cyclic structure with one or more straight-chain monoolefinic compounds having 2 to 10 carbon atoms by one or more phenol resins, as herein defined, in the presence of one or more halides, preferably chlorides, of one or more metals of Groups II or III of the Periodic Table or halides of a heavy metal, said heavy metal having a specific gravity greater than 4 or a mixture of halide precursors for any such halide or halides as herein defined. The Periodic Table used is that of Lothar Meyer

and Mendelejeff.

Alternatively, the copolymer may be derived from one or more polyolefinically unsaturated compound, partly or wholly of cyclic structure and one or more branched chain mono-olefinic compounds.

The copolymers may, alternatively, be derived from a mono-olefin component containing up to 90 mol per cent, calculated on the total mono-olefin component, of one or more branched mono-olefinic hydrocarbons having 4 to 12 carbon atoms.

The fact that such copolymers may be cross-linked according to the invention by the substances in question is fundamentally new and very important insofar as these copolymers have properties completely different from butyl rubber and other elastomers. For example, they are quite different from butyl rubber in that they are very much less branched. The copolymers to be cross-linked according to the invention may contain double bonds either in the main chains or in side chains.

The polyolefinically unsaturated compound may be cyclic or acyclic or mixtures of such compounds. The proportion of cyclic compound in the polyolefinically unsaturated compound mixture may be at least 10, preferably at least 50 mol per cent. Usually these compounds will be dienes and, moreover, preferably those having conjugated double bonds. The polyolefinically unsaturated compound may contain the group $\text{CH}_2=\text{C}<$.

Specific examples of acyclic dienes have the formula $\text{CH}_2=\text{CH}-\text{CR}^1=\text{CH}_2$ in which R^1 is hydrogen, methyl, ethyl, propyl, chlorine, fluorine, acetoxy, chloroacetoxy, butyroxyl or cyano radical, e.g. butadiene, isoprene, 2,3-dimethyl-butadiene-1,3, 1,2-dimethyl-butadiene-1,3, 1,3-dimethyl-butadiene-1,3, 1,4-dimethyl-butadiene-1,3, 1-ethyl-butadiene-1,3, 2-ethylbutadiene-1,3, 2-propylbutadiene-1,3, 2-chlorobutadiene-1,3, 2-fluoro-butadiene-1,3, 2-acetoxy-butadiene-1,3, 2-chloroacetoxy-butadiene-

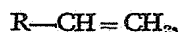
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1,3, 2 - butyroxylbutadiene - 1,3 and 2 - cyano-butadiene - 1,3, further, for example, piperylene, hexadiene - 1,3, 2- or 4 - methyl - pentadiene - 1,3, tetradecadiene - 1,3, 2 - phenyl-1,3 - butadiene or 1 - phenyl - 2,3 - dimethylbutadiene - 1,3. Examples of suitable cyclic compounds are cyclopentadiene and dicyclopentadiene. The proportion of the diene-component in the copolymer is generally 0.5 to 10, preferably 1 to 5 mol%.

The mono - olefinic compounds used are straight chain mono - olefins with from 2 to 10 carbon atoms or, in the indicated specific embodiments, branched mono - olefins with from 4 to 12, preferably from 4—7 carbon atoms. The proportion of branched mono-olefins used in a mixture of mono - olefins may be up to 90 mol per cent, generally from 10 to 70 and preferably up to 50 mol per cent, calculated on the total mono - olefins present.

Specific examples of suitable mono - olefins are ethylene, propylene, butene-1, pentene-1, hexene - 1, heptene - 1, octene - 1 and decene-1. Branched olefins, which may be used in the process of the present invention include, for example, isobutylene, its dimers or trimers and 1-ethyl-1-methylethylene.

The copolymers used in the present invention may be produced by any known process and may be made from olefin mixtures. Thus, for example, copolymers may be made from a mixture containing at least 20 mol% ethylene, an α - olefin of the formula

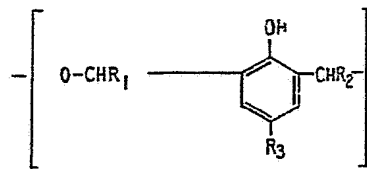


in which R means an alkyl radical with 1 to 8 carbon atoms and 0.5 to 10 mol% of dicyclopentadiene.

By the term phenolic resin in this Specification we mean a resin made by condensing an aldehyde and a phenol in an alkaline medium and having at least one free, or esterified phenolic-hydroxy group and at least one free, etherified or esterified alcoholic hydroxy group or at least one halogen atom instead of said free, etherified or esterified hydroxy groups. The phenolic resins will generally be used in an amount from 1 to 15, preferably 3 to 9 parts by weight per 100 parts of unsaturated copolymer. For example, suitable phenol resins are those in which two of the three o,o,p-positions, preferably the two o-positions (with respect to the phenolic hydroxy group) of a mononuclear phenol are substituted on reaction with an aldehyde. This is possible if the phenol resins are derived from mononuclear phenols which contain a substituent in one of the o,o,p-positions to the phenolic hydroxy group, preferably in p-position. Preferably this substituent is a hydrocarbon radical. It may, however, be another radical, which does not inhibit condensation in an o-position, for example, halogen such as chlorine, nitro or

cyano. Phenol resins derived from phenols having all of the o,o,p-positions with respect to the phenolic hydroxy group free and containing substituents having a total of at least 4 carbon atoms in the m-positions to the phenolic hydroxyl groups may be used in like manner. If the phenols contain more than one substituent, these may be the same, or different. Preferably the substituents are hydrocarbon radicals with 1 to 12 carbon atoms such as the methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, isobutyl or tert-butyl, the straight-chained, branched or cyclic primary, secondary or tertiary pentyl, hexyl, heptyl, octyl, decyl, or dodecyl radical, for example the tert-amyl radical, the normal or isooctyl radical such as the ethylhexyl or diisobutyl radical; or cyclohexyl, benzyl or phenyl radicals which may be substituted with an alkyl radical, e.g. methylcyclohexyl, tolyl or xylyl. Preferably all substituents in a given phenol together contain 1 to 12 carbon atoms and if the substituents are in a position para to the phenolic hydroxy group, 4 to 12 carbon atoms. These substituents may themselves be substituted with chlorine or bromine, as may for example the phenolic nucleus.

Other phenol resins suitable for use in the process of this invention are formed by cyclic condensation of phenoldialcohols. Such cyclic condensates may be used alone or as mixtures of condensation products, which contain these cyclic portions in an amount of, for example, at least 85 per cent by weight. To facilitate the incorporating of these products into the copolymers it is advisable to use them together with agents aiding the dispersion, e.g. the plasticizers mentioned below. The cyclic condensates may be built up from 3, 4 or more phenolic nuclei and have the general formula



in which R_1 and R_2 may be the same or different. (Generally R_1 and R_2 are hydrogen or an alkyl radical with 1 to 3 carbon atoms, for example methyl, or a furyl radical) and R_3 is one of the radicals mentioned above for substituents in the o,o,p-positions. The symbol n is at least 2 and indicates how many phenol nuclei are combined to form a ring. Preferably n is 3 to 5, but it may also be higher, for example 8.

The production of cyclic condensates in which R_3 is an alkyl radical with 4 to 12 carbon atoms is particularly simple. The

formation and properties of cyclic condensates of this type, for example from *p* - tert.-butyl phenol and *p* - octylphenol are described in "Kunststoffe", 52 (1962), 19—21.

- 5 Other phenol resins which may be used according to the invention are the so-called trifunctional resins which are resins, which have been obtained from trifunctional phenols —i.e. phenols, with three free positions *o*,*o*,*p*-
10 to the phenolic hydroxy group by reaction with an aldehyde, for example phenol, *m*-cresol or homologues such as *m*-xylenol in an alkaline medium. Still further phenol resins which may be used according to the invention are
15 so-called diphenol resins. These may be produced by condensation of a dihydric phenol such as resorcinol or a binuclear dihydric phenol in an alkaline medium with an aldehyde. Suitable dihydric phenols are dihydroxy
20 diphenyl, dihydroxy dibenzyl, dihydroxy diphenylmethane, or homologues thereof, e.g. dihydroxy diphenyl - methyl - methane, -dimethyl - methane, -ethyl - methane,
25 -methylethyl - methane, -diethyl - methane, -methylpropyl - methane, -dipropyl - methane, -methylhexyl - methane, -dihexylmethane or -methyl - cyclohexyl - methane, or products substituted in the phenyl nuclei such as the 3-methyl, 3,5 - dimethyl or 3,3¹ - diisopropyl
30 substitution products. Diphenols containing the two hydroxy groups in the 4,4¹ - positions are especially preferred.

- Aldehydes, which may be reacted with the above-mentioned phenols are especially those
35 with 1 to 7 carbon atoms such as acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, crotonaldehyde, benzaldehyde, furfural or mixtures of two or more such aldehydes. The preferred aldehyde is formaldehyde. These
40 aldehydes may also be reacted with mixtures of two or more phenols.

The resulting resins may be used per se, but they may also be modified.

- The alcoholic hydroxyl groups formed in the
45 resins may thus be etherified or esterified either before or during the condensation of the phenols with the aldehyde. Etherification is preferably carried out using monohydric alcohols and to such an extent that the resins
50 are still soluble in organic solvents. Suitable monohydric alcohols are, for example, methyl, ethyl, propyl, isopropyl, butyl, octyl, isooctyl, dodecyl, or benzyl alcohols. Esterification is preferably effected with monobasic carboxylic
55 acids, such as acetic acid, propionic acid or butyric acid. The etherification or esterification modifies the reactivity of the resins so that subsequent autocondensation of the resins is reduced or completely prevented, thus favouring
60 cross-linking of the resins with the polymer chains. The resins may also be modified by replacing the alcoholic hydroxy groups with halogen. For example chloromethyl groups may be introduced in the *o*- and/or *p*-position
65 to the phenolic hydroxyl group. The phenolic

hydroxyl group may also be esterified, for example with the above-mentioned monobasic carboxylic acids.

The partially etherified or esterified resins may be further modified by plasticizing. Thus, the resins may be reacted at a temperature above 70°C with a hydroxy fatty acid which contains more than 10 carbon atoms or a glyceride thereof, so that a resin, which is still soluble in organic solvents is obtained. The resins may also be plasticized under similar conditions with glyceride oils, or oil-modified alkyd resins such as esters of polyhydric alcohols with a mixture of (A) dicarboxylic acids and (B) either fatty or resin acids or a mixture of fatty and resin acids. The production of such plasticized resins is described in British Patent Specification No. 409,397.

The phenol resins are usually semi-solids. They may conveniently be used in solution with varying amounts of solvents conventionally used in the varnish industry, such as butanol, benzene, toluene, or xylene or in solution in compounds which are useful as plasticizers for rubbers, for example, mineral oils, aliphatic or aromatic polyethers, esters of polybasic carboxylic acids, polyglycols, polyhydric alcohols or mixtures of two or more of these. These compounds may be monomeric or polymeric in nature. The varnish-type solvents may be replaced by the rubber-plasticizer compounds by mixing the mixtures of the resins and the varnish type-solvents with a suitable amount, e.g. 10 to 50% by weight, of the rubber plasticizer compound and distilling off the varnish-type solvent at reduced pressure, preferably at a temperature below 100°C.

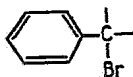
As metal halides, it is preferred to use chlorides and bromides, especially stannous chloride, an iron chloride or an iron bromide. However, other halides, such as stannous iodide or the chlorides and bromides of the metals mentioned below may also be used. Basic halides such as Sn(OH)Cl are also suitable.

The effect of the metal halides may be increased by the addition of fillers, especially active or semi-active carbon black. If the metal halides per se are incorporated directly into the copolymer mixture, the compounding and processing procedures are rendered more difficult since the metal halides are not easily incorporated into the copolymer mixture and may also cause considerable corrosion. It is, therefore, more desirable to produce the metal halides *in situ* in the copolymer mixture during mixing, by reacting a halogen-donor and a metal compound capable of reacting with the halogen-donor at elevated temperature e.g. at a temperature above 70°C. The term "halogen-donor" is used to denote an organic compound from which halogen or hydrogen halide may be split off. The halogen-donor and the metal compound are termed halide precursors.

Halogen-donors include, for example, poly-

mers or copolymers of vinyl chloride and/or vinylidene chloride with other polymerisable compounds, preferably those which contain no stabilising agent; halogen containing polymers, for example polychloroprene; halogenated, for example chlorinated or brominated butyl rubber; halogenation or chlorosulphonation products of high density or low density polyethylene or higher polyolefins; colloidal mixtures of polyvinyl chloride with an acrylonitrile - butadiene copolymer; halogenated hydrocarbons containing halogen atoms which may be split off or which may split off hydrogen halide, for example liquid or solid chlorination products of paraffinic hydrocarbons of natural or synthetic origin; halogen containing factice; benzyl chloride, benzal chloride or benzotrichloride or homologues thereof, heptachlorocyclohexane; chlorinated acetic acids; acid halides, for example lauroyl, oleyl, stearyl or benzoyl chlorides or bromides, diphenyl bromomethane, diphenyldibromomethane or triphenylbromomethane, benzotribromide and compounds which contain the group NHal, in which Hal represents halogen, for example N-bromosuccinimide or N - bromo - phthalimide or mixtures of two or more such compounds. Bromo - compounds such as these containing the structure

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have been found to be particularly effective.

In order to form the metal halides, compounds of the following metals may be used; magnesium, cadmium, calcium, beryllium, zinc, lead, manganese, cobalt, nickel, antimony and, especially, tin and/or iron. These metals may be used in the form of oxides or, in the case of chromium, titanium or aluminium, in the form of compounds, e.g. as salts of weak inorganic or organic acids such as formic, acetic, lauric, stearic, benzoic, chromic, silicic and carbonic acids. Basic salts of the acids may also be used. Furthermore, mixtures of two or more of these compounds may be used. Especially good results have been obtained by using iron salts of one of the above acids, e.g. stearic acid, if desired in mixture with stannous or zinc compounds.

The amount of halogen-donor and metal compound used in the mixture depends on their halogen and metal content respectively and the ease with which the halogen or hydrogen halide is split off. The amount of these compounds used also depends on the desired degree and conditions of vulcanization. Generally, they are used in an amount such that 0.1 to 12, preferably 0.3 to 6 parts by weight of metal halide, based on 100 parts of the copolymer, are present or may be formed. However, smaller or larger amounts of halogen-

donor and metal compound may be added, depending on the desired results. The ratio of metal compound, such as the zinc oxide, to halogen-donor may be varied within wide limits, and either the amount of metal compound or halogen-donor may be in excess of the other. For example, the metal compound may be added in such an amount that the amount of halogen or hydrogen halide is only sufficient to form a basic metal halide. When the metal halide is formed *in situ* in the mixture, a strong activation of the vulcanization may be obtained by heating the mixture prior to the addition of the resin, for a short time, for example, for a period of 5 to 20 minutes, to a temperature between 70 and 250°C, preferably between 120°C and 220°C. During the heat-treatment the metal halide is formed, thus increasing the vulcanization rate and the vulcanization effect.

The selection of the type and the amount of the metal halide and the halogen or the hydrogen halide donor respectively and the conditions of the heat treatment which give the optimum amount of the metal halide in the copolymer and best results of the vulcanisation can be determined by preliminary trial.

If the copolymer mixture is compounded on roll mills the heat treatment is generally carried out for a period up to 15 minutes for economic reasons. The metal halide may, however, also be added or the metal compound be reacted with the halogen-donor while storing or ageing the mixture at a temperature in the indicated range for a longer period, e.g. from 30 to 90 minutes.

The reaction of the halogen-donor and the metal compound may also be effected by mixing some or all of the ingredients of the mixture to be vulcanized, for example, in an internal mixer such as a Banbury mixer, at the aforesaid temperature. In this procedure it is not necessary to conduct the whole mixing procedure at said temperature, it being sufficient to keep the mixture at that temperature only for a period sufficient to allow reaction between the metal compound and the halogen-donor. The formation of the metal halides in the copolymer may also occur in two stages, i.e. in part in the compounding procedure at the normal compounding temperature and in part during the vulcanization.

In carrying out the invention the copolymer, the resin, the metal halide and the other components may be compounded in any desired order according to the usual procedures adopted in the preparation of rubber mixtures. If a metal halide is added, the vulcanizing resin should be added and incorporated as late as possible in order to avoid premature vulcanization of the mixture. It is also possible to mix the metal halide with phenol resin and then react it therewith by gently heating the mixture, which procedure facilitates the incorporation of the metal halide into the vul-

canization mixture and improves the vulcanization effect. If the metal halide is to be produced *in situ* from a metal compound it is advantageous to incorporate the metal compound and the halogen-donor in the mixture first, in order to provide a good distribution of these components in the plastic so as to ensure that the greatest possible amount of metal halide is formed. Any additional components, for example, stearic acid, palmitic acid, myristic acid or lauric acid or other auxiliary substances, may then be added.

The starting products used according to the invention may also be mixed with plastomers or elastomers before cross-linking them, for example, with polymers or copolymers of ethylene, propylene, isobutylene or butyl rubber, natural rubber, polyisoprene, polybutadiene, copolymers of butadiene with acrylonitrile and/or styrene, polychloroprene. Generally the proportion of such an additional component will not be higher than 50 per cent by weight.

If, in order to improve the activating effect of the metal halide, the mixture is heated to above 120°C and placed for a short while between rolls or kneaded or stored, it is preferable to add the resin used as vulcanizing agent only after the mixture has cooled.

It is also possible to add before or during

the heat treatment a small amount of a resin acting as cross-linking agent, e.g. about 0.1 to 1.5 parts for every 100 parts. In this case, some cross-linking occurs during the heat-treatment which affects the compounding process only slightly.

The mixture may be vulcanized and moulded by any convenient procedure, for example, by heating in hot air or steam at temperatures above 100°C, for example up to 220°C, or by pressing in heated moulds. It is preferred to effect the vulcanization at temperatures between 150 and 170°C and for periods of 5 to 60 minutes. In order to shorten the vulcanization process, it is possible to work at temperatures of above 170°C. Generally, the mixtures may be prepared while using fillers such as carbon black or lightly coloured fillers, e.g. active silicic acid. The products obtained may be used for the manufacture of commercial rubber goods, e.g. sole material, tyres, inner tubes, packing sheets, door mats and shock absorbers and cable insulations.

In order that the invention may be well understood the following examples are given by way of illustration only:—

EXAMPLE I—III

The following mixtures were produced:

| Mixture | I | II | III |
|---|-----|-----|-----|
| ethylene-propylene-dicyclopentadiene rubber with about 3.5-4 double bonds per 1000 carbon atoms | — | 100 | — |
| ethylene-propylene-dicyclopentadiene rubber with about 5 double bonds per 1000 carbon atoms | 100 | — | 100 |
| high abrasion furnace carbon black (HAF-grade) | 45 | 45 | — |
| super abrasion furnace carbon black (ISAF-grade) | — | — | 45 |
| stearic acid | 1 | 1 | 2 |
| $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ | 3 | 4 | 3 |
| Resin A | 6 | — | — |
| Resin B | — | 6 | 10 |

5 The carbon black and the rubber are milled together and the stearic acid, the stannous chloride and the resin are then incorporated, one after another, into this mixture. The order of the additions may, however, be modified. The mixture was produced at 90—100°C, but the use of higher or lower tem-

peratures is also possible. The resins were produced by condensation, in an alkaline medium, of formaldehyde with *p*-tert.-butylphenol (Resin A), or with *p*-octylphenol, respectively (Resin B). The mixture is then vulcanized at 160°C and the following values obtained:—

10

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| Mixture | I | | | II | | III | |
|---|-----|-----|-----|-----|-----|-----|-----|
| Vulcanisation time (min.) | 40 | 60 | 90 | 60 | 90 | 60 | 90 |
| Tensile strength (kg/cm ²) | 100 | 130 | 134 | 102 | 117 | 133 | 144 |
| Elongation at break (%) | 380 | 361 | 323 | 432 | 349 | 319 | 285 |
| Modulus 150 (kg/cm ²) | 24 | 30 | 38 | 18 | 24 | 41 | 50 |
| Modulus 300 (kg/cm ²) | 71 | 98 | 121 | 58 | 91 | 125 | — |
| Permanent elongation (%) | 31 | 22 | 13 | 33 | 18 | 12 | 10 |
| Impact resistance (kg/cm ²) | 13 | 11 | 13 | 16 | 10 | 12 | 10 |
| Hardness (°Shore A) | 62 | 63 | 64 | 60 | 62 | 65 | 68 |
| Rebound elasticity (%) | 45 | 46 | 46 | 47 | 45 | 37 | 37 |

As filler, silica may also be used instead of carbon black. In this case the amount of the resin is desirably increased to about 8 to 12 parts.

20 1. Permanent elongation is the percentage increase of the predetermined length of the standard ring R I (DIN 53 504) immediately after tearing.

25 2. Impact resistance is the resistance against tearing further measured at the standardized ring R II (DIN 53 504) having three notches.

In these, and the following examples, all tests were made using standardized rings in

which the distance between the inner and outer radii is 4 mm, the rings having a thickness of 6 mm.

EXAMPLE IV

This example illustrates vulcanization using a reaction product of *p*-dodecylphenol-dialcohol and SnCl₂·2H₂O. Products of this type may be obtained, according to Patent Specification No. 880,756, by dissolving *p*-dodecylphenol - dialcohol and SnCl₂·2H₂O in acetone and heating slightly. The product contains about 28% Sn and 16% Cl.

35

40

| Mixture | IV |
|--|-----|
| ethylene-propylene-dicyclopentadiene-copolymer as described in Example III | 100 |
| stearic acid | 1 |
| reaction product of dodecylphenol-dialcohol and SnCl ₂ ·2H ₂ O | 6 |
| super-abrasion furnace carbon black (SAF-grade) | 45 |
| Resin from <i>p</i> -octylphenol and formaldehyde (prepared by condensation in an alkaline medium) | 6 |

The mixture was prepared as described in Examples I to III
 Vulcanization temperature: 160°C.

| Mixture | IV | |
|--|-----|-----|
| Vulcanization time (min.) | 60 | 90 |
| Tensile strength (kg/cm ²) | 98 | 122 |
| Elongation at break (%) | 348 | 316 |
| Modulus 150 (kg/cm ²) | 31 | 39 |
| Modulus 300 (kg/cm ²) | 81 | 112 |
| Permanent elongation (%) | 25 | 16 |
| Impact resistance (kg/cm) | 13 | 10 |
| Hardness (°Shore A) | 64 | 65 |
| Rebound elasticity (%) | 38 | 37 |

EXAMPLES V—VIII

- 5 These examples illustrated activation of the vulcanization by metal salts of organic acids and compounds from which halogen or hydro-

gen halide may easily be split off. The mixtures are rolled for about 10 minutes before the addition of the phenol resin.
 Test results of the vulcanisates:

10

| Mixture | V | VI | VII | VIII |
|---|-----|-----|-----|------|
| ethylene-propylene-dicyclopentadiene-copolymer as described in Example III | 100 | 100 | 100 | 100 |
| stearic acid | 1 | 1 | 1 | — |
| diphenylbromomethane | 3 | 3 | 3 | — |
| N-bromo-succinimide | — | — | — | 2.5 |
| iron stearate | 2 | 2 | 2 | 2 |
| tin stearate | — | — | 1 | — |
| super-abrasion furnace (SAF) carbon black | 45 | 45 | 45 | 45 |
| Resin from <i>p</i> -isooctylphenol and formaldehyde (obtained by condensation in an alkaline medium) | 6 | 6 | 6 | 10 |

Manufacture of the mixtures:

The copolymer is first rolled out on the mill until a sheet is formed. Then the other ingredients of the mixture are incorporated with exception of the phenol resin. The order in which the ingredients of the mixture are introduced is not important. In this procedure the temperature of the mixture is about 90°C. The mixture is then removed and placed on a rolling mill with heated rolls. After the formation of the sheet care was taken to ensure that the temperature of the mixture is between 130 and 250°C (measured with a commercial pyrometer). The mixtures

are then hot rolled for 10 minutes at the following temperatures:—

| | |
|--------------|-----------|
| Mixture V | 160—180°C |
| Mixture VI | 175—180°C |
| Mixture VII | 170—180°C |
| Mixture VIII | 160—165°C |

The mixtures are taken off while still hot and are mixed in a third working step with the phenol resin the mixing temperature being about 90°C.

Vulcanization temperature 160°C.
Test results of the vulcanisates

| Mixture | V | | VI | | VII | | VIII | |
|--|-----|-----|-----|-----|-----|-----|------|-----|
| Vulcanisation time (min.) | 60 | 90 | 60 | 90 | 60 | 90 | 60 | 90 |
| Tensile strength (kg/cm ²) | 149 | 132 | 141 | 150 | 123 | 131 | 111 | 129 |
| Elongation at break (%) | 328 | 286 | 358 | 353 | 374 | 375 | 446 | 400 |
| Modulus 150 (kg/cm ²) | 28 | 32 | 24 | 24 | 20 | 21 | 14 | 17 |
| Modulus 300 (kg/cm ²) | 127 | — | 101 | 111 | 83 | 87 | 52 | 74 |
| Permanent elongation (%) | 12 | 11 | 17 | 13 | 20 | 22 | 28 | 21 |
| Impact resistance (kg/cm) | 7 | 6 | 11 | 9 | 10 | 10 | 13 | 11 |
| Hardness (°Shore A) | 57 | 58 | 56 | 57 | 56 | 57 | 55 | 55 |
| Rebound elasticity (%) | 43 | 43 | 40 | 40 | 41 | 40 | 40 | 41 |

The manufacture of the mixtures described in Examples V—VIII can be considerably simplified by milling in an internal mixer. The effect otherwise attained by rolling at higher temperatures for a longer time may then be obtained by kneading at suitable temperatures for a short time. The resin used as vulcanization agent may, be incorporated at the end of the milling, if the milling time required therefor is so short that no vulcanization occurs. The examples further show the suitability of an iron stearate, as well as of diphenylbromomethane, for the vulcanization of the types of rubber according to the invention. Vulcanisates with a good vulcaniza-

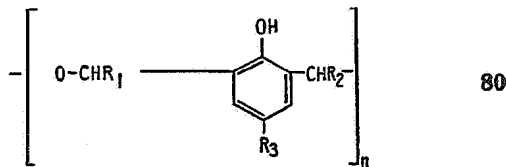
tion level may also be obtained by simultaneous addition of an iron- and tin- or zinc stearate.

Care should be taken to ensure that the metal and the halogen-containing compounds are used in a suitable ratio. By using too large an amount of halogen-containing substance depolymerisation of the ethylene-propylene - copolymer may occur during milling. Mixtures which have deteriorated in this way are no longer vulcanisable.

WHAT WE CLAIM IS:—

1. A process for cross-linking unsaturated copolymers comprising vulcanizing one or more copolymers which have been obtained by the

- copolymerisation of one or more polyolefinically unsaturated compounds having 4 to 14 carbon atoms with one or more straight-chain-mono - olefinic compounds having 2 to 10 carbon atoms by one or more phenol resins, as herein defined in the presence of one or more halides of one or more metals of Groups II or III of the Periodic Table (per Meyer and Mendelejeff) or halides of a heavy metal, said metal having a specific gravity greater than 4 or a mixture of halide precursors for any such halide or halides as herein defined.
2. A modification of the process as claimed in claim 1 wherein the copolymer is derived from one or more cyclic polyolefinically unsaturated compounds and one or more branched chain mono - olefinic compounds.
3. A process as claimed in either of the preceding claims wherein the polyolefinically unsaturated compound is a diene.
4. A process as claimed in any of the preceding claims, wherein the polyolefinically unsaturated compound contains a pair of conjugated double bonds.
5. A process as claimed in any of the preceding claims, wherein the copolymers used are prepared from hydrocarbon monomers.
6. A process as claimed in any of the preceding claims, wherein the polyolefinically unsaturated compound is cyclic and contains a ring of five carbon atoms.
7. A process as claimed in any of the preceding claims, wherein the copolymer used contains from 0.5 to 10 mol% of a diene component.
8. A process as claimed in claim 7, wherein the copolymer contains from 1 to 5 mol% of a diene component.
9. A process as claimed in any of the preceding claims, wherein the phenol resin is used in an amount from 1 to 15 parts by weight for every 100 parts by weight of copolymer.
10. A process as claimed in claim 9, wherein the phenol resin is used in an amount from 3 to 9 parts by weight for every 100 parts by weight of copolymer.
11. A process as claimed in any of the preceding claims, wherein the phenol resin used is a condensation product of a phenol and an aldehyde having 1 to 7 carbon atoms.
12. A process as claimed in claim 11, wherein the phenol resin used is a trifunctional phenol resin, as herein defined.
13. A process as claimed in claim 11, wherein two of the three positions, ortho, ortho and para to the phenolic hydroxy group are unsubstituted.
14. A process as claimed in claim 13, wherein the two positions ortho to the phenolic hydroxy group are free.
15. A process as claimed in claim 13 or 14, wherein the remaining of the three positions is substituted with a hydrocarbon radical with 4 to 12 carbon atoms.
16. A process as claimed in claim 15 wherein the phenol is *p* - octylphenol, *p* - tert-butylphenol or *p* - isooctylphenol.
17. A process as claimed in claim 11, wherein the phenol resin is a condensation product of an aldehyde with a phenol substituted in at least one position meta to the phenolic hydroxy group with a group which contains at least 4 carbon atoms.
18. A process as claimed in claim 11 or claim 13, wherein the phenol resin used is a condensation product which contains at least 85% by weight of cyclic phenol aldehyde condensation products of the formula:—



in which R_1 and R_2 are hydrogen or an alkyl radical with one to three carbon atoms, or a furyl radical, and in which R_1 and R_2 are the same or different radicals and in which R_3 is a hydrocarbon radical with 1 to 12 carbon atoms, chlorine, nitro or cyano and n is an integer from 2 to 8.

19. A process as claimed in claim 18, wherein n is an integer from 3 to 5.

20. A process as claimed in any of claims 11 to 19, wherein the phenol resin used is a condensation product of an aldehyde with a dihydric phenol.

21. A process as claimed in claim 20, wherein the dihydric phenol is a binuclear phenol.

22. A process as claimed in any of claims 11 to 21, wherein the phenol resin used is a condensation product of an aldehyde with a mixture of more than one phenol.

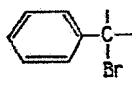
23. A process as claimed in any of claims 11 to 22, wherein the aldehyde is formaldehyde.

24. A process as claimed in any of claims 11 to 23, wherein the phenol resin used is plasticised by heating to a temperature above 70°C with a hydroxy fatty acid containing more than 10 carbon atoms or a glyceride thereof; a glyceride oil; or an ester of a polyhydric alcohol with a mixture of (A) dicarboxylic acids and (B) fatty acids and/or resin acids.

25. A process as claimed in any of claims 11 to 24, wherein the phenol resin is used in solution in a solvent conventionally used in the varnish industry.

26. A process as claimed in any of claims 11 to 25, in which the phenol resin is used in solution in one or more compounds useful as plasticizers for rubbers.

27. A process as claimed in any of claims 1

- to 26, wherein the metal halide used is a chloride or bromide.
28. A process as claimed in any of claims 1 to 27, wherein the metal halide used is mixed with a phenol resin and chemically combined therewith before adding it to the mixture to be vulcanized.
29. A process as claimed in any of claims 1 to 28, wherein the metal halide is produced in situ in the mixture to be vulcanized prior to or during the vulcanization by reaction between one or more halogen-donors as herein defined and one or more metal compounds capable of reacting therewith at a temperature above 70°C.
30. A process as claimed in any of claims 1 to 29, wherein the mixture to be vulcanized is heated prior to the addition of the phenol resin to a temperature from 70—250°C.
31. A process as claimed in claim 30, wherein the mixture is heated to a temperature of from 120°C to 220°C.
32. A process as claimed in any of claims 29 to 31, wherein the halogen-donor used is a bromo compound.
33. A process as claimed in any of claims 1 to 32, wherein the metal halide used is stannous chloride or an iron chloride.
34. A process as claimed in any of claims 1 to 33, wherein the metal halide or the halogen-donor and the metal compound reactive therewith are used in an amount such that 0.1 to 12 parts by weight of the metal halide are contained or may be formed in the mixture to be vulcanized for every 100 parts of the elastomer.
35. A process as claimed in claim 34, wherein the metal halide or the halogen donor and the metal compound reactive therewith are used in an amount such that 0.3 to 6 parts by weight of the metal halide are contained or may be formed in the mixture to be vulcanized for every 100 parts of the elastomer.
36. A process as claimed in any of claims 1 to 35, wherein before the vulcanization step is carried out, up to 50% by weight of one or more other copolymers is admixed with the original copolymer, the percent figure being calculated on the total weight of the mixture of the elastomers.
37. A process as claimed in claim 36, wherein butyl rubber is added.
38. A process as claimed in any of claims 1 to 37, wherein the mixture to be vulcanized is heated to a temperature above 70°C and is admixed prior to or during this heat treatment with 0.1 to 1.5 parts of a phenol resin for every 100 parts of the elastomer.
39. A process as claimed in any of claims 1 to 38, wherein one or more fillers are added to the elastomer or elastomers prior to the vulcanization.
40. A process as claimed in claim 39, wherein the filler used is carbon black.
41. A modification of the process claimed in any of claims 1 to 40, wherein copolymers are vulcanized in which the monoolefin component contains up to 90 mol %, calculated on the total mono - olefin component, of one or more branched monoolefinic hydrocarbons having 4 to 12 carbon atoms.
42. A process as claimed in claim 41, wherein one or more of the branched mono - olefinic hydrocarbons used contains from 4 to 7 carbon atoms.
43. A process as claimed in either of claims 41 and 42, wherein the proportion of branched mono-olefin used is from 10 to 70 mol %.
44. A process as claimed in any of claims 41 to 43, wherein the proportion of branched mono-olefin used is from 10 to 50 mol%.
45. A process as claimed in any of claims 1 to 44, wherein the poly-olefinically unsaturated compound used contains at least 50 mol% of a cyclic compound.
46. A process as claimed in any of claims 1 to 45, wherein the poly-olefinically unsaturated compound used is dicyclopentadiene.
47. A process as claimed in any of claims 1 to 46, wherein the metal halide used is produced in the mixture by reacting a metal compound with a compound containing the group:—
- 
- and being capable of splitting off bromine or hydrogen bromide.
48. Vulcanization products when made by the process claimed in any one of claims 1 to 47.
49. Shaped bodies containing or comprising vulcanization products as claimed in claim 48.
- For the Applicants,
FRANK B. DEHN & CO.,
Chartered Patent Agents,
Imperial House,
15/19 Kingsway,
London, W.C.2.